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BOSTON UNIVERSITY

GRADUATE SCHOOL

Dissertation

THE ADSORPTION OF HYDROGEN BY CHARCOAL

by

Thomas Davis Phillips

(A.B., Oberlin College, 1916

S.M., University of Michigan, 1923)

submitted in partial fulfilment of the

requirements for the degree of

Doctor of Philosophy

1934

H.E.F.

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## O U T L I N E

THE PROBLEM	Page 1
A HISTORICAL SURVEY	Page 3
THE APPARATUS	Page 8
THE METHOD	
A. General Procedure	Page 11
B. Variations in Procedure	Page 13
C. Difficulties in Procedure	Page 16a
THE RESULTS AND THEIR INTERPRETATION	Page 17
A THEORETICAL DISCUSSION OF THE PROBLEM	Page 27
SUMMARY	Page 34
BIBLIOGRAPHY	Page 36
AUTOBIOGRAPHY	Page 39



OUTLINE

Page 1	THE PROBLEM
Page 3	A HISTORICAL SURVEY
Page 8	THE APPARATUS
	THE METHOD
Page 11	A. General Procedure
Page 13	B. Variations in Procedure
Page 16	C. Difficulties in Procedure
Page 17	THE RESULTS AND THEIR INTERPRETATION
Page 27	A THEORETICAL DISCUSSION OF THE PROBLEM
Page 34	SUMMARY
Page 36	BIBLIOGRAPHY
Page 38	AUTOBIOGRAPHY



## THE PROBLEM

The phenomena of sorption are attributed to two distinct processes; namely,

a. A relatively rapid process known as adsorption, which is recognized as a surface phenomenon.

b. A much slower process known as absorption, which is explained either as the dissolving of the sorbed material by the sorbent with the formation of a solid solution, or as the diffusion of the sorbed substance into the interior pores of the sorbent, followed by adsorption on the internal surfaces.

The work here described was undertaken as an investigation of the adsorptive (a) part of the sorption process. Adsorption, as is generally recognized, proceeds rapidly, and therefore any information relative to this part of the sorption process must be based on data concerning the conditions which arise very shortly after the substance to be sorbed is exposed to the action of the sorbent. Such data have been lacking.



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distinct processes; namely,

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In order to gain the desired information, a preliminary study of the rate of sorption of certain gases on activated charcoal, especially during the very early part - - the first two or three minutes - - of the sorption process, was undertaken in 1925-1927.

Pressure-time sorption curves were obtained, using the gases, air, nitrogen, and hydrogen, and under certain conditions some very interesting and peculiar curves of results could be plotted. In 1927 a report of the experimental work was written (unpublished) and an hypothesis advanced that would explain the presence of the peculiar effects from the standpoint of the process of adsorption. At that time, however, it was not known just what variation in the treatment of the charcoal produced the variation in the shape of the curves.

Hence, further research was undertaken, and completed during the past year, to confirm the original hypothesis and to obtain additional data which would answer this question of variation.



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## A HISTORICAL SURVEY

Investigation of the early part of the sorption process, as partially completed in 1927, had led to the advancement of the hypothesis that the process of adsorption of hydrogen by charcoal consisted in a spreading of "puddles" of the adsorbed gas over the surface of the charcoal. This theory will be explained in detail in a later section.

Since that time other experimenters have reported results which tend to confirm these conclusions. At the meeting of the American Physical Society, November 1927, George E. Read reported he had found that a slow-moving stream of lithium atoms was regularly reflected from a "clean" (gas-free) platinum surface. Consistent results were obtained only when the platinum reflector had been heated white hot not more than a few seconds before each reading. Readings with a hot surface gave the same results as for a cold surface.

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course of the discussion they stated that this reflection could not be accomplished with a glass surface. No interpretation of these effects was offered, but it appears reasonable to ascribe the difference between the glass and the crystal to the fact that the adsorbed film of gas cannot be completely removed from the glass. This is in accord with the fact that Read's results were with a non-crystal surface which by the very high temperature had been rendered gas-free.

Taking the two experiments into account we see that lack of regularity in arrangement of surface atoms could not of itself cause the failure of specular reflection. It would seem obvious that adsorption and subsequent diffuse re-evaporation of the streams of atoms or molecules prevented the appearance of specular reflection in the case of a surface whose condition would admit of adsorption; that is, one with some gas already present to start with. A further study of these phenomena as an indication of adsorption effects should prove of interest and value.

J.H.Frazer reports an optical study of adsorbed films. \* The presence of a gas film on a reflecting surface will cause plane-polarized light to be elliptically polarized after reflection, when certain optical conditions are met. By

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causing plane-polarized light to fall upon a surface freshly prepared in vacuum and determining the ellipticity of the reflected light he was able to follow the growth of adsorbed gas upon the surface. In a study of adsorption of water vapor by this means he concludes that adsorption occurs as a growth of "clusters".

Because of its definite bearing upon the problem under discussion, the more recent work of Benton and White on the adsorption of hydrogen by certain metals is quoted below at length, as is also the comment on this work by Allmand and Burrage.

\* "We have been led to advance a new hypothesis of physical adsorption according to which the observed steps represent the formation of concentric rows of adsorbed molecules, first at the edges of each crystal face and building up successively toward the center. The evidence in support of this hypothesis rests primarily on the uniformity in the volumes corresponding to the successive steps and to the actual magnitude of the individual step.

"The mechanism by which adsorption can occur in successive rows may readily be derived on the assumption that neighboring adsorbed molecules evaporate from the surface less readily than isolated molecules and that physically adsorbed molecules possess mobility in the plane of the

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The work on which these conclusions were based was a study of adsorption of hydrogen on copper, nickel and iron. The experimental procedure was also of a quite different nature from that under consideration. The conclusions are, therefore, not applicable in their entirety. The similarity between their assumptions and the hypothesis herewith presented is, nevertheless, rather striking. These conclusions they have supported by work which they have reported. \*

Finally, to quote from A.J.Allmand and L.J.Burrage, Kings College, London University, September 28, 1931.\*\*

"We shall await with much interest the further details of the results on discontinuities in adsorption isothermals forecasted in the communication recently made by Messrs. Benton and White. In particular the hypothesis offered in explanation of discontinuous phenomena attracts our attention as it is similar in certain respects to one which we were seriously considering about two years ago. The following is an extract

\*Jour. Am. Chem. Soc. Vol. 53, 3301-14 (1931)

" " " " Vol.54, 1373-90 (1932)

" " " " Vol.54, 1820-30 (1932)

Trans.Faraday " Vol.28, 202-18 (1932)

\*\*Jour. Am. Chem. Soc.Vol.53, 4453 (1931)







from a report of a lecture given by one of us in the University of Oxford in December 1929:

"The speaker finally briefly discussed possible explanations for the discontinuous structure of these isothermals which his experiments seemed to make probable. As a working hypothesis (for there are difficulties and objections to be overcome and far more experimental work is needed) he inclined to the following. Adsorption on charcoal starts out from "active centers" from which islands of sorbate spread out. An island is actually composed of a series of concentric rings. - -"



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R = Reservoir F = Furnace  
 M = Manometer  
 P = Photographic Recorder  
 H = Charcoal Bulb  
 E = Auxiliary Charcoal Bulb  
 A, B, C, D = Stopcocks

Supply of Gas  
to be studied

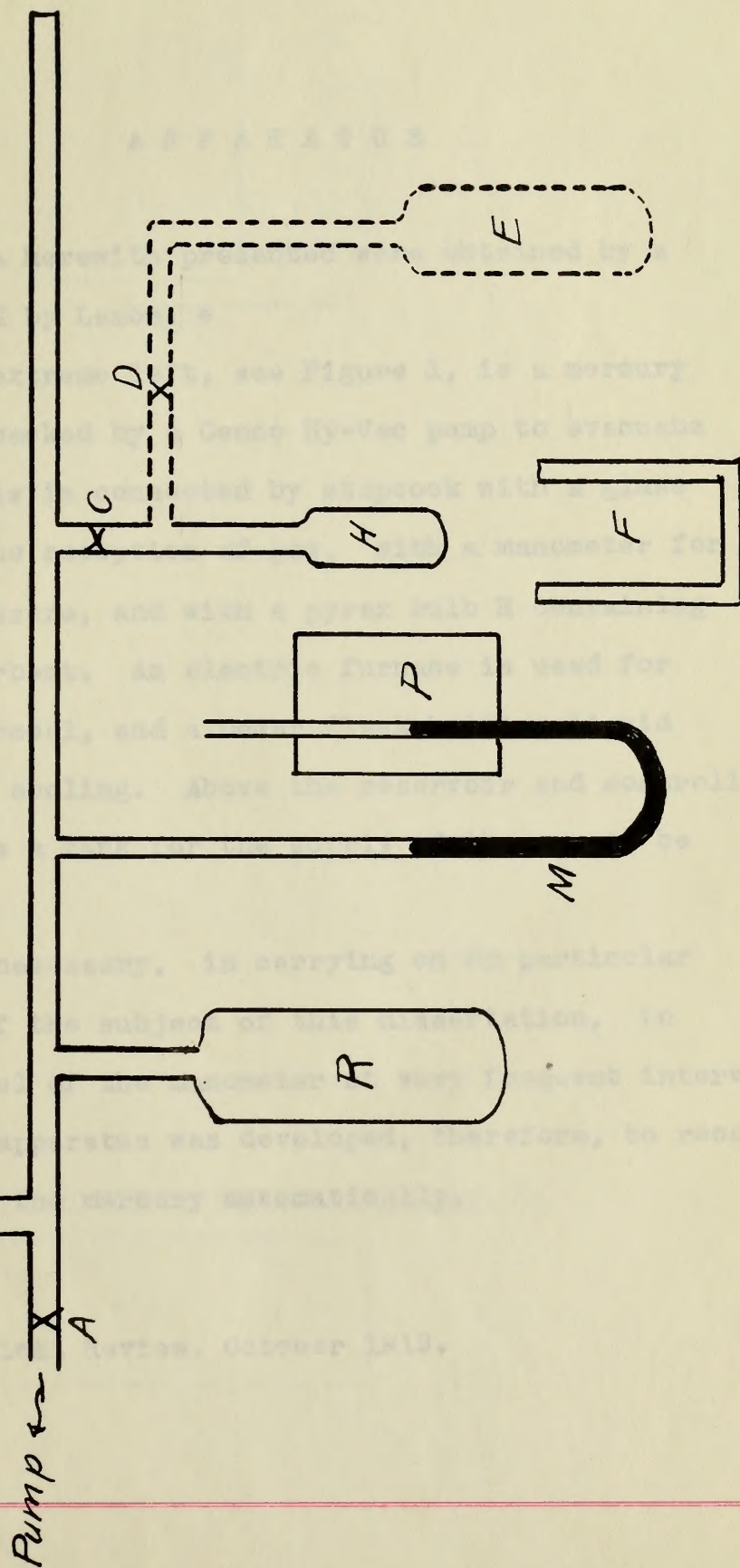


Figure 1.







## A P P A R A T U S

The data herewith presented were obtained by a method described by Lemon. \*

At the extreme left, see Figure 1, is a mercury diffusion pump backed by a Cenco Hy-Vac pump to evacuate the system. This is connected by stopcock with a glass reservoir for the reception of gas, with a manometer for reading the pressure, and with a pyrex bulb H containing the charcoal sorbent. An electric furnace is used for heating the charcoal, and a Dewar flask holding liquid oxygen, for its cooling. Above the reservoir and controlled by a stopcock is a tank for the supply of the gas to be studied.

It was necessary, in carrying on *the* particular investigation of the subject of this dissertation, to measure the level of the manometer at very frequent intervals. A photographic apparatus was developed, therefore, to record the readings of the mercury automatically.

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P = Box containing photographic paper

M = Manometer

n-n = narrow slit

S = Shutter

H = Lamp House

L = Light Source

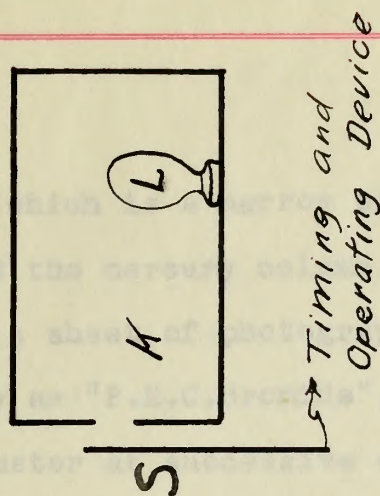
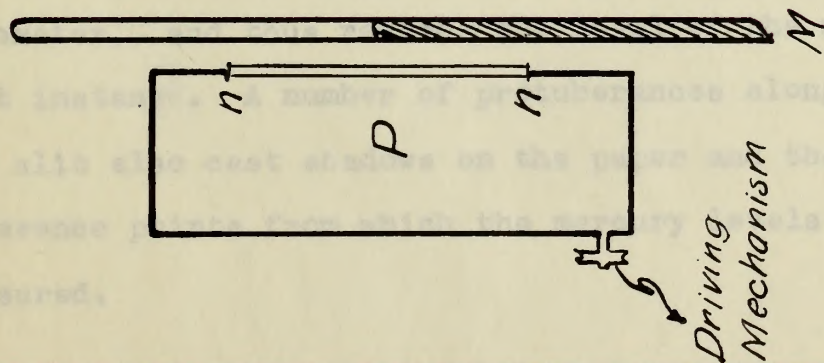
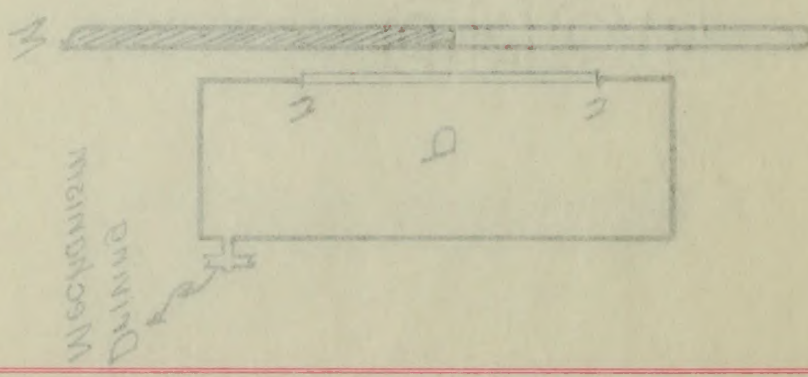


Figure 2.



Figure 5.



Mechanical Device

Operating Device  
and Limiting and



$L = \text{light source}$   
 $A = \text{actuator}$   
 $S = \text{switch}$   
 $M = \text{mechanism}$   
 $D = \text{device}$



A box, in which is a narrow slit, is placed immediately behind the mercury column of the manometer. Within the box is a sheet of photographic paper, 15" x 20", known commercially as "P.M.C.Bromide". The record of the level of the manometer at successive equal time intervals is recorded on the photographic paper - - as it is pulled horizontally past the slit by a driving mechanism - - by flashes of light emanating from the light source, shown in Figure 2.

K is a light-tight box with an opening which may be closed by the shutter S. In the work of 1926-27 this shutter was operated electrically so as to give light flashes of very short duration at regularly timed intervals. In the work of the past year a mechanical shutter timed by a pendulum was used for this purpose.

The light shining upon the manometer passes through the slit in the box P and falls upon the moving photographic paper. The image formed upon the paper shows a shadow over that part of the slit covered by the mercury in the manometer, and thus records the level of the mercury at that instant. A number of protuberances along the edge of the slit also cast shadows on the paper and these serve as reference points from which the mercury levels can be measured.



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Additional apparatus is found necessary for carrying on a part of the work, as will be explained later. This consists of a large auxiliary bulb containing charcoal, connected with the original bulb and used to prepare the original charcoal for the admission of the gas. A second electric furnace is also used at this period in the research.

All the more recent work was done with the same weight, twenty-five grams, of the same kind of charcoal, steam-activated, prepared by the Carbide and Carbons Chemical Corporation.

The hydrogen used was prepared by electrolysis of NaOH solution, using nickel electrodes. The resulting gas was purified by passing over platinized asbestos and calcium chloride.

Next, the bulb B is immersed in liquid oxygen and some time later C is opened. Immediately before opening the stopcock C, however, the photographic recorder of the manometer readings is set in operation.

In the first work on this problem the shutter S, in Figure 2, was adjusted to give flashes of one-fifth second (calibrated) at five-second intervals. In the work of the past year the time interval was one and one-half seconds with an exposure of less than one-tenth second.



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## THE METHOD

### A. General Procedure

Referring to Figure 1:

The stopcock B is closed. Stopcocks A and C are opened and the electric furnace is placed around H. The pump is started and the pumping and heating continue simultaneously for a length of time to be indicated later.

Then stopcocks A and C are closed, the electric furnace is removed from H, and the gas to be adsorbed is admitted by opening stopcock B, filling R and the system with the exception of H. B is then closed.

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### 3. Variations in Procedure

A record is made of the manometer readings for the first two to five minutes of the sorption process. After the resulting exposed photographic paper is developed, the progressive decrease in pressure of the gas, due to the sorption, is plotted against time by taking off the manometer levels to graph paper by the use of dividers.

Various temperatures were used. The duration of outgassing and admission of the gas to the bulb of charcoal was also varied.

The nature of the results obtained in this exploratory work led, step by step, to the development of the standardized details of procedure, with certain variations, which produced the final and definitely significant nine runs.

The pressure-time curves for the nine runs were obtained using 25 grams of the steam-activated charcoal, from Carbide and Carbon Chemical Corporation, as mentioned previously. The time of outgassing was six hours. The temperature of outgassing in all these cases was 500 degrees C. Electrolytic hydrogen as prepared by electrolysis was the gas used. Adsorption took place with the bulb immersed



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## B. V a r i a t i o n s i n P r o c e d u r e

A total of sixty-six runs was made and recorded. Of these, all but the last nine may be considered, for present purposes, as exploratory.

Varying temperatures were used. The duration of periods of outgassing varied. Different kinds and amounts of charcoal were tried. Runs were made employing, respectively, nitrogen, air and hydrogen as the gas to be studied. Tank hydrogen and electrolytic hydrogen were used. The length of time allowed to elapse between cessation of outgassing and admission of the gas to the bulb of charcoal was also varied.

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in liquid oxygen.

The chief variants in procedure in the case of these different runs were, the length of time elapsing after the cessation of outgassing and the length of time during which the charcoal bulb was immersed in liquid oxygen prior to the admission of hydrogen to the bulb. These times are recorded in Table A, below:

TABLE A

T i m e i n M i n u t e s

I

II

Run No.	From immersion in liquid O to admission of H	From cessation of outgassing to admission of H <sub>2</sub>
1	1½	6½
2	12	25
3	3	36
4	1	52
5	1¾	11
6	2 1/6	8
7	12	15
8	1	30
9	? (not known)	1½

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Time in Minutes

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1	1 1/2			6 1/2
2	1 1/2			2 1/2
3	3			3 1/2
4	1			6 1/2
5	1 1/2			1 1/2
6	2 1/2			8
7	1 1/2			1 1/2
8	1			30
9	?	(not known)		1 1/2



Aside from these differences in time, there were variations in the sequence of operations after turning off the heat of the furnace about H.

For runs 3, 4, 5, 6, 8 and 9, the order of operations, referring to Figure 1, was as follows:

- a. Turn off heat and remove furnace.
- b. Close stopcock C.
- c. Close stopcock A.
- d. Admit hydrogen to reservoir R by opening and then closing again stopcock B.
- e. Place charcoal bulb in liquid oxygen.
- f. Start camera box and light-flasher.
- g. Open stopcock C, admitting hydrogen for sorption.

Time elapsing between operations e and g is recorded in column I of TABLE A, and that between operations a and g is recorded in column II.

Run 7 differed from the above in that the stopcock C was left open to the rest of the system during the cooling with liquid oxygen. That is, the order of operation was a, c, e, b, d, f, g.

Runs 1 and 2 illustrate another variation in treatment. A large auxiliary charcoal bulb E was used in preparing the bulb H for these runs. During the process of

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outgassing H a second furnace was placed around bulb E and the stopcock D was left open so that both bulbs were outgassed. E was outgassed for four hours; H for six hours. Two hours before the completion of the outgassing of H the furnace was removed from E and the stopcock D was closed.

The bulb E was cooled in liquid oxygen and, at the close of outgassing of H, stopcock C was closed and stopcock D was opened. The charcoal in E thus served to clean up the residual gas and created a condition highly favorable to the production of a relatively gas-free surface.

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### C. D i f f i c u l t i e s   i n   P r o c e d u r e

Aside from those problems which are ordinarily confronted in work which involves the outgassing of charcoal, there were a few unique to this particular experiment.

In the earlier work an attempt was made to read the manometer directly. This method was found unsatisfactory because of the haste with which such readings had to be taken, and the consequent <sup>of</sup>danger inacc<sup>u</sup>racies. To avoid these inaccuracies the photographic method, described in a previous section, was devised.

A separate investigation was found necessary to determine the proper size of tube for the manometer. If the tube were too large, oscillations of the mercury after the first fall lasted so long that it was impossible to begin taking readings as early as was desirable. On the other hand, if the tube were too small, manometer lag became troublesome. It was found that a tube of .24cm. inside diameter was nearly critically damped, so this was the size chosen.







Figure 3







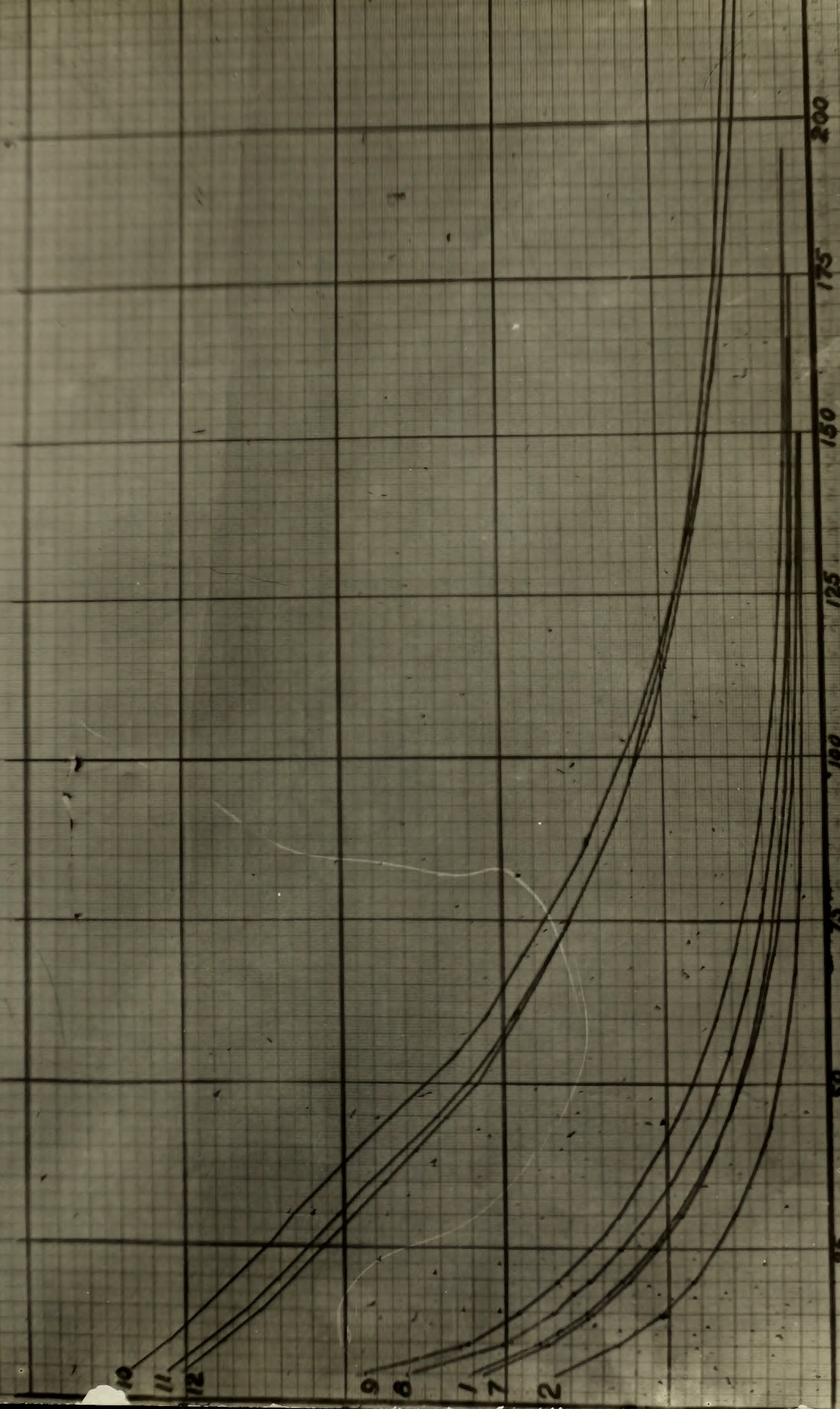


Figure 4

Time - Seconds







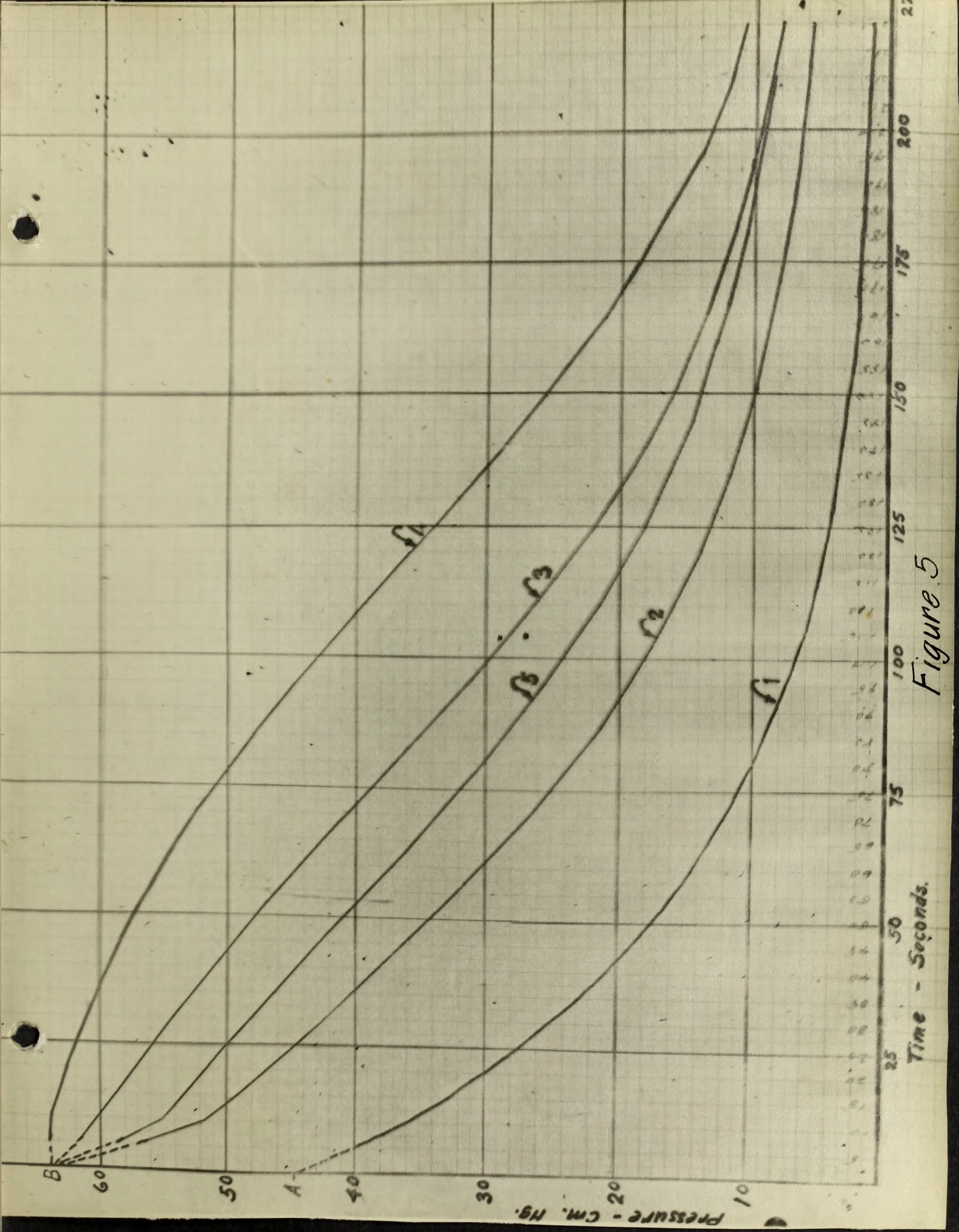


Figure 5

Time - Seconds.





## RESULTS AND THEIR INTERPRETATION

In Figure 3 is a reduced copy of a typical photographic record from which the results have been compiled.

In Figure 4 are shown curves of which ##1 and 2 are for air; ##7, 8 and 9 are for nitrogen; and ##10, 11 and 12 are for hydrogen. These early runs led to the choice of hydrogen as the gas to be particularly investigated, as its action is slower and therefore offers more possibility of obtaining the information desired concerning the early stages of the sorption process.

In Figure 5 are shown curves of which #1 is for nitrogen and ##2, 3, 4 and 5 are for hydrogen. In all five of these the time and temperature of outgassing and the charcoal used were identical.

Curve #4 indicates definitely a sorption which is slow at first and increases with the lapse of time. An upward convexity occurs in the early part of the curve.

Curve #2, on the other hand, shows decreasing sorption throughout and is concave upward throughout.



# RESULTS AND DISCUSSION

In Figure 1 is a typical plot of a typical photo-  
graphic record showing the reaction rate between

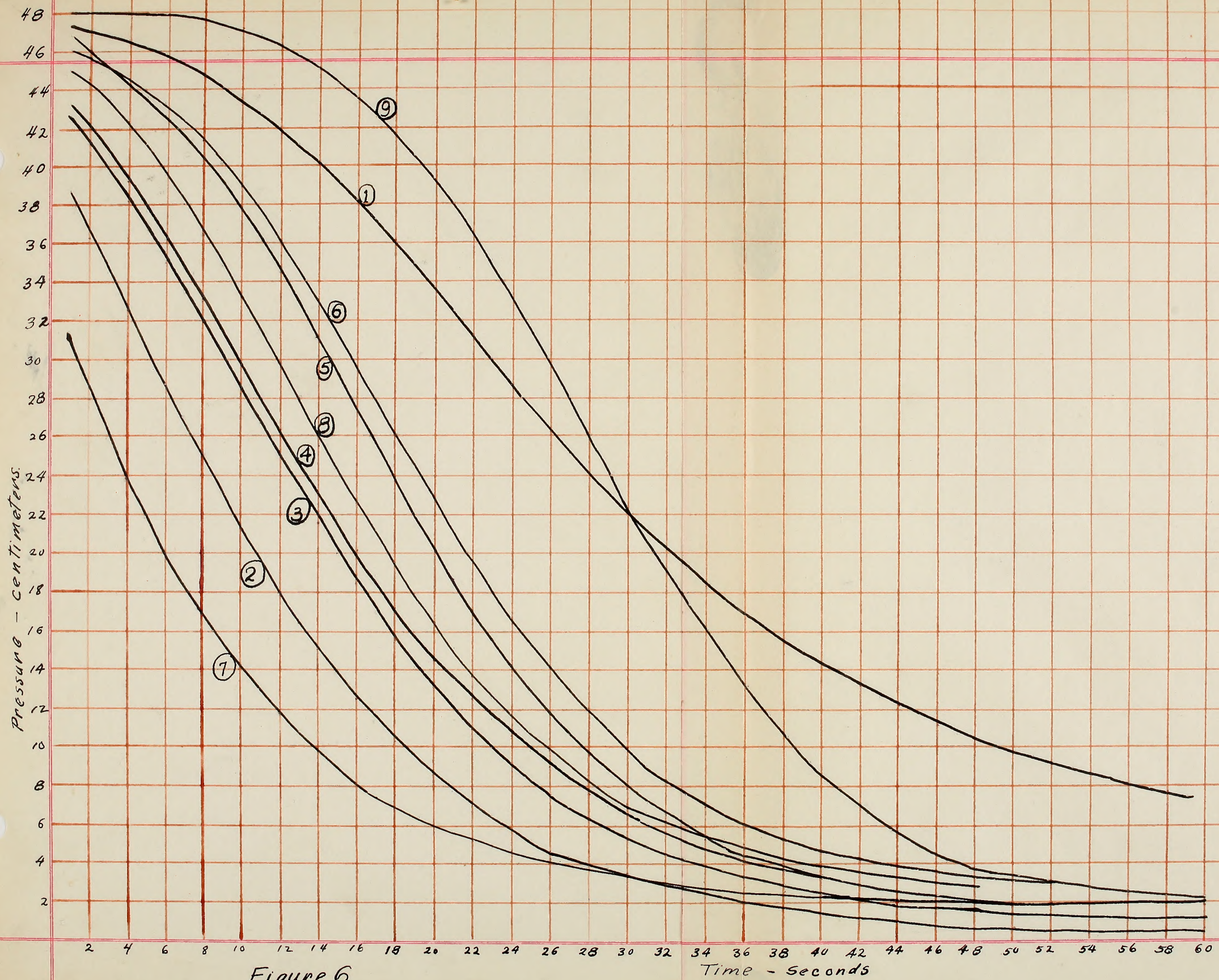
In Figure 2 are shown curves of  $\log \frac{1}{1-x}$  and  $\log \frac{1}{1-x}$

for the reaction between hydrogen and nitrogen at 400°C. and 450°C. The curves are linear, indicating that the reaction is of first order with respect to hydrogen and second order with respect to nitrogen. The slopes of the curves are 1.0 and 2.0, respectively, indicating that the reaction is of first order with respect to hydrogen and second order with respect to nitrogen. The intercepts of the curves are 0.0 and 0.0, respectively, indicating that the reaction is of first order with respect to hydrogen and second order with respect to nitrogen.

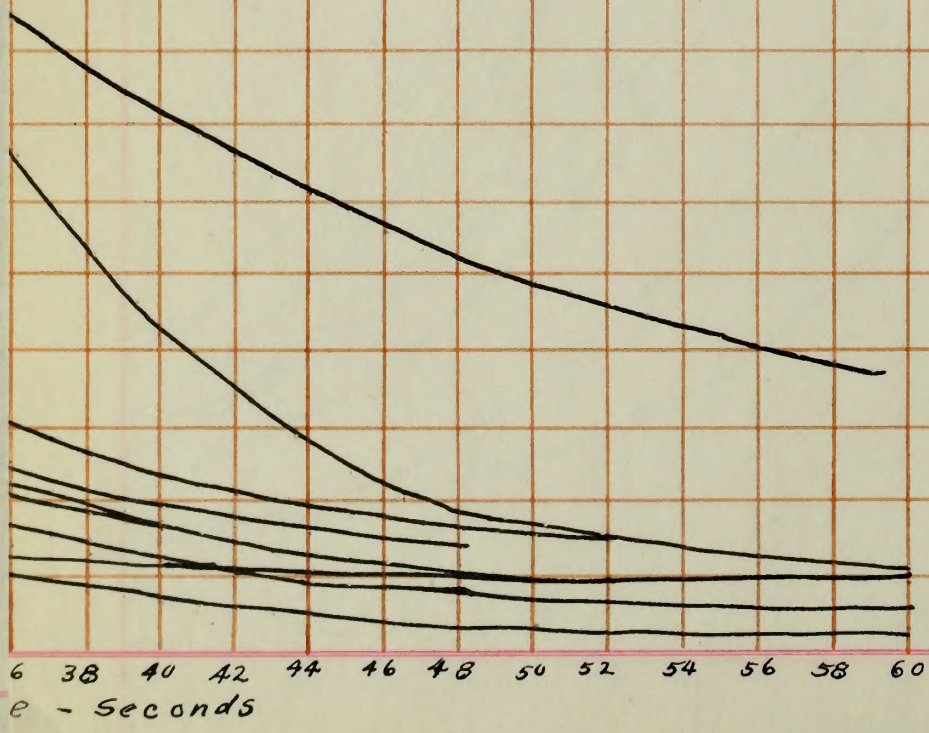
In Figure 3 are shown curves of  $\log \frac{1}{1-x}$  for  
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of these cases the curves are linear, indicating that the  
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second order with respect to nitrogen.

Figure 4 is a plot of  $\log \frac{1}{1-x}$  versus time for  
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Curves ##3 and 5 represent an intermediate condition.

The results here given are shown not to have arisen from differences in the method of outgassing or in the charcoal used, since these conditions were the same for all four.

We turn, then to a detailed discussion of the curves in Figure 6, which were drawn from the data of the final nine runs of the later work and which do establish conclusively the variations in conditions which lead to a delayed adsorption and hence to contrasting curves.

As noted in a previous section, the amount and kind of charcoal, the temperature and duration of outgassing, the source of hydrogen, were the same for all nine runs. In all these cases, also, the charcoal bulb was immersed in liquid oxygen before sorption was started.

These curves show the upward convexity in varying degree. The conditions within the system are changing very rapidly during this early part of the process and a number of circumstances which affect the rate of fall of pressure are listed below:



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degrees. The conditions within the system are changing very

rapidly during this early part of the process and a number

of circumstances which affect the rate of fall of pressure

are listed below:



1. The heat of adsorption causes local increases in temperature and tends therefore temporarily to raise the pressure.

2. There is a difference in pressure at various parts of the tube, due to the flow of the gas.

3. Local cooling and heating due to the semi-adiabatic volume changes, under turbulent conditions, affects the manometer reading.

4. The increase in volume, due to the expansion of the gas into the vacuous space surrounding the charcoal, itself causes a fall in pressure.

5. There is a lag in the manometer reading.

6. The cooling of the gas from the room temperature of the reservoir to the liquid oxygen temperature causes a fall in pressure.

7. The ratio of para- to ortho-hydrogen changes when the hydrogen passes from the reservoir at room temperature to the charcoal bulb at liquid oxygen temperature.

It is not possible to eliminate these effects, but they cannot be the cause of the variations in the form of the curve since they would always be present to approximately the same degree if the sorption were otherwise the same in all cases.



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We must search, then, for the cause of these variations, in the difference in treatment and procedure during the interval between the cessation of the outgassing and the introduction into the charcoal bulb of the gas which is to be sorbed. For convenience in referring to this interval we shall designate it as T. Similarly, t will indicate the time between immersion of the charcoal bulb in liquid oxygen and the admission of hydrogen. From TABLE A the data are retabulated below in a changed order:

TABLE A'

Run No.	I Time, t, in minutes	II Time, T, in minutes
9	?	$1\frac{1}{2}$
6	$2\frac{1}{6}$	8
5	1	11
8	1	30
4	1	52
3	3	36
-----		
7	12	15
1	$1\frac{1}{2}$	$6\frac{1}{2}$
2	12	25



We must search, then, for the cause of these variations, in the difference in treatment and procedure during the interval between the cessation of the outgassing and the introduction into the charcoal bulb of the gas which is to be sorbed. For convenience in referring to this interval we shall designate it as T. Similarly, t will indicate the time between immersion of the charcoal bulb in liquid oxygen and the admission of hydrogen. From TABLE A the data are retabulated below in a changed order:

TABLE A'

Run No.	I	II
	Time, t, in minutes	Time, T, in minutes
9	?	1½
6	2 1/8	8
5	1	11
8	1	30
4	1	52
3	3	36
-----		
7	12	15
1	1½	6½
2	12	25



In TABLE A', the charcoal used in making the runs indicated by curves ##9, 6, 5, 8, 4, 3, received identical treatment during the interval T, except that there was the variation of the times, T and t, as shown. These curves are arranged in this table in the order of decreasing upward convexity.

For ##5, 8 and 4, t is the same. It is evident, then, that the difference in the form of the curves is due to the difference in the total time, T.

The positions of curves ##3 and 6, with their greater lengths of time-interval t, reveal the influence of variation in this interval.

If we compare #3 with #4 we note that its value of T would place it between #4 and #8, but it falls, on the contrary, slightly below #4 in the experimentally determined curves. This due, then, to increased length of time t, and we may conclude that an increase in duration of either T or t will lower the first part of the curve and decrease its upward convexity.

This conclusion is borne out by a comparison of #6 with #5. In #6 the time T is less than that for #5, so that we would expect it to fall above #5, as it does. The greater time t, however, tends to make the fall lower, with the result that it is only slightly higher than #5 and of



In TABLE A', the charcoal used in making the runs indicated by curves #4, 5, 6, 7, 8, 9, 10, received identical treatment during the interval T, except that there was the variation of the times, T and t, as shown. These curves are arranged in this table in the order of decreasing upward convexity.

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a slightly greater upward convexity.

These differences in the curves may have either one of two interpretations. We may ascribe them to a failure of the charcoal to cool to the same low temperature on account of the difference in time allowed for cooling. This would, however, not account for the marked difference between #8 and #4, since the time allowed for cooling to room temperature in both these cases was so great that only a very little difference in temperature could possibly exist at the time of immersion in liquid oxygen, and the additional time of cooling in liquid oxygen was the same in both cases.

The other interpretation, which is borne out by the discussion of the remaining data, is that the charcoal, when allowed to stand after cessation of outgassing, adsorbs some of the residual gas. The adsorption will of course proceed more rapidly if the charcoal stands immersed in liquid oxygen in the meantime. We may propose that a relatively gas-free surface will yield a curve of the form #6, and that as the amount of initially adsorbed residual gas increases, the curve form changes progressively to that of #3.



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of #8.



This interpretation is also in accord with the shape of an individual curve such as #6. We note that when the gas is at first brought into contact with the charcoal the rate of adsorption is small but increases with the passage of time. This means that the adsorption of some of the gas puts the charcoal into such a condition that it adsorbs more readily additional hydrogen.

Both the shape of the individual curves and the treatment that results in a different curve lead to the same conclusion, that a charcoal surface upon which there already exists some adsorbed gas is a better adsorbing surface than one that is more nearly clean.

As adsorption proceeds, however, a time will of course be reached when the decreasing pressure and decrease in available area will cause a decrease in rate of sorption. This point will be discussed in more detail in a later section.

With this interpretation in mind, we come now to an examination of the remaining curves. In obtaining curves ##1 and 2 the charcoal was prepared by a method calculated to remove, in a greater degree, the chance of the surface accumulating a layer of initially adsorbed gas from the residue present in the system upon the cessation of outgassing.



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This was accomplished by means of the extra charcoal tube previously described. While the charcoal sample was standing after the outgassing, the previously outgassed and cooled charcoal in the auxiliary tube was connected to the sample bulb, and so served to remove residual gas from that bulb. In this way the likelihood of obtaining an initial relatively gas-free surface was increased for these two runs.

In run #1 both  $t$  and  $T$  are slightly less than for #6. The difference in form of curve between #1 and #6 is, however, too great to make it appear at all plausible that this difference is due to the differences in  $t$  and  $T$  alone. The greater delay of adsorption due to the relatively higher degree of gas removal is in this case notable.

Curve #2 resulted from immersion of the charcoal in liquid oxygen for 12 minutes and can best be compared with the neighboring curve #7, which represents immersion in liquid oxygen for the same length of time. In other respects than the duration of  $t$  and  $T$  the treatment of the charcoal during the interval  $T$  was varied as greatly as possible, in these two cases.



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Curve #2 resulted from immersion of the charcoal in liquid oxygen for 15 minutes and can best be compared with the neighboring curve #7, which represents immersion in liquid oxygen for the same length of time. In other respects than the duration of  $t$  and  $T$  the treatment of the charcoal during the interval  $T$  was varied as greatly as possible, in these two cases.



In the case of #2 the stopcock C was closed immediately after outgassing was completed and the stopcock D, into the auxiliary charcoal bulb, was opened. In this way the residual gas was reduced to a minimum. In the case of #7, on the other hand, the stopcock C was left open until it was necessary to close it in order to fill the reservoir with hydrogen. In this case, then, an opportunity was given to the sample of charcoal to adsorb residual gas from the whole system. In other words, the charcoal for making these two runs was prepared in such a way that, for the times allowed, there would be the least possible opportunity given in #2 for adsorption of residual gas, while in #7 there would be the greatest possible opportunity for such adsorption.

The result, as shown in the curves, is further proof that the cleaner surface (#2) adsorbs less readily at first than the surface with more adsorbed residual gas (#7). It is interesting to note that the curves cross (at 29 seconds) as would be expected since the more nearly gas-free surface will eventually adsorb a greater amount of gas.



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It may also be noted that although the times  $t$  in liquid oxygen are equal, the time  $T$  was greater for #2 than for #7, which would tend to establish the reverse relationship from the one found. This, then, emphasizes the significance of the measures taken.

In curve #9 the total time  $T$  was very short, and the result is in accord with others found. The time here, however, was too short to make this run significant in itself; but comparison of #9 with #1 is significant, since #9 represents the maximum effect that may be obtained by shortening the times  $t$  and  $T$ . The fact that #1 crosses #9 is further evidence that the shape of #1 is due in part to the use of the extra tube and the resultant decrease in residual gas.



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In curve  $\#3$  the total time  $T$  was very short, and the result is in accord with others found. The time here, however, was too short to make this run significant in itself; but comparison of  $\#3$  with  $\#1$  is significant, since  $\#3$  represents the maximum effect that may be obtained by shortening the times  $t$  and  $T$ . The fact that  $\#1$  crosses  $\#3$  is further evidence that the shape of  $\#1$  is due in part to the use of the extra tube and the resultant decrease in residual gas.



A T H E O R E T I C A L   D I S C U S S I O N  
O F   T H E   P R O B L E M

We may conclude that a nearly gas-free surface does not accumulate atoms of gas by adsorption as readily as a surface upon which some gas is already present. The process is not unlike precipitation from a solution or condensation of a vapor from a supersaturated solution. Adsorption will occur most readily on a surface which is already "wet", but not saturated, with a gas.

The process may be pictured as follows: The surface is nearly but not completely freed from adsorbed gas. It is spotted with atoms or clusters of atoms one layer thick. The gas to be adsorbed is exposed to this surface. An atom which strikes the surface near one of the already existent groups is itself adsorbed. We then have a surface on which are puddles of adsorbed gas, with areas expanding as adsorption proceeds. As the puddles grow larger the adsorption at first goes faster because of the increasing length of boundary. Then, as the puddles begin to combine and run into each other, the length of the boundary decreases and the rate of adsorption decreases also.

Figure 7



## A THEORETICAL DISCUSSION OF THE PROBLEM

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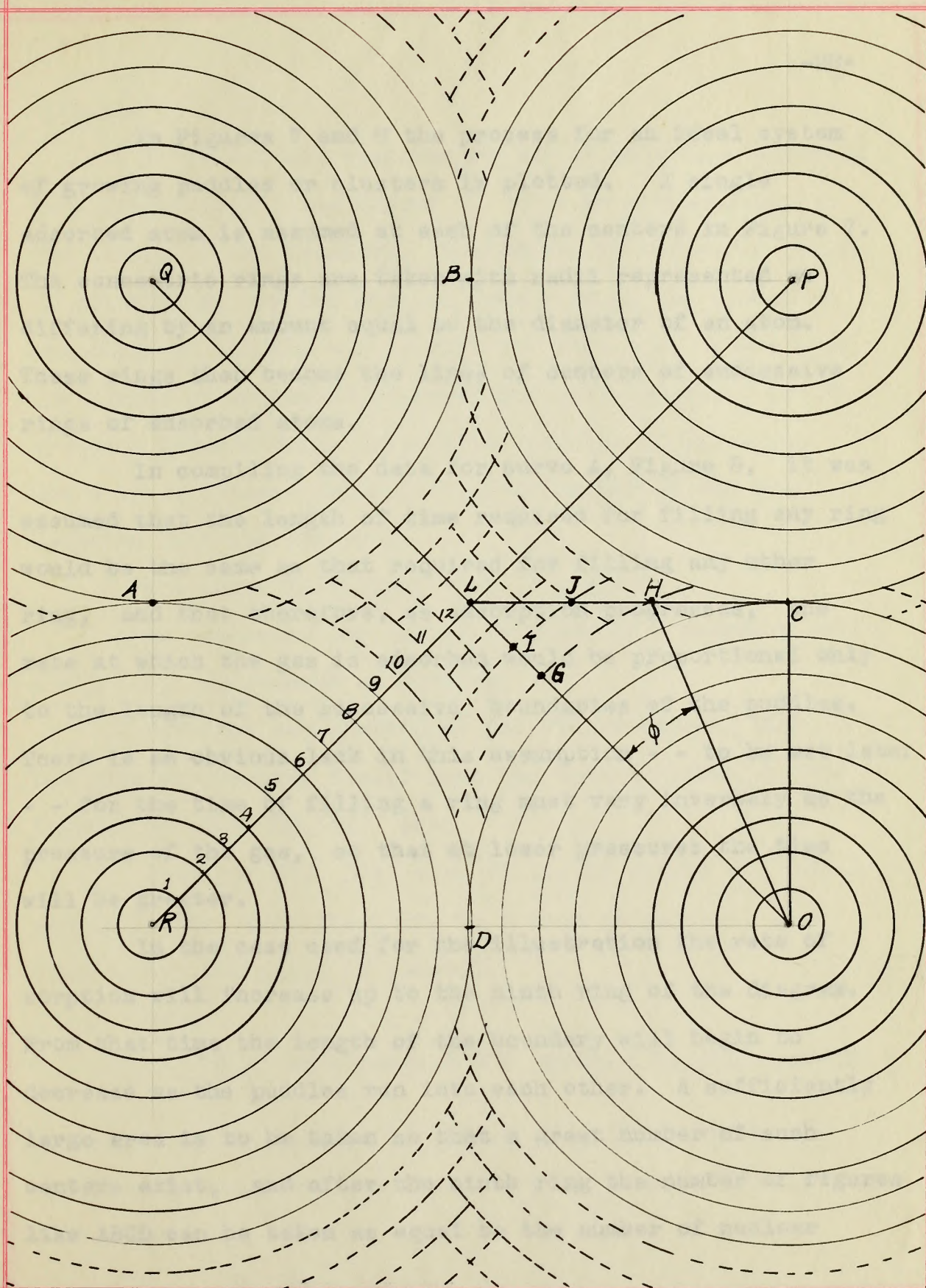


Figure 7.



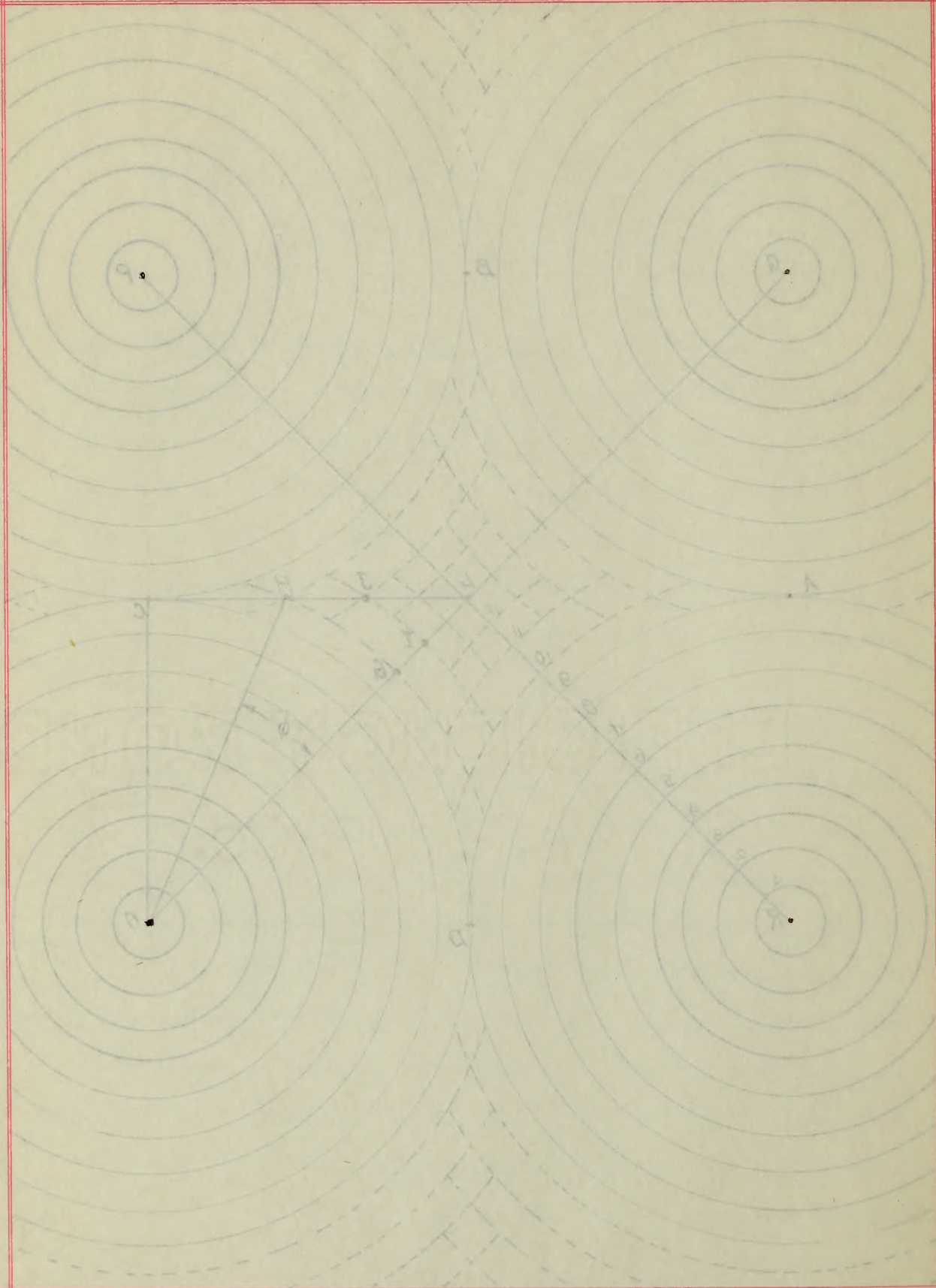


Figure 7.



In Figures 7 and 8 the process for an ideal system of growing puddles or clusters is plotted. A single adsorbed atom is assumed at each of the centers in Figure 7. The concentric rings are taken with radii represented as differing by an amount equal to the diameter of an atom. These rings then become the lines of centers of successive rings of adsorbed atoms.

In compiling the data for curve A, Figure 8, it was assumed that the length of time required for filling any ring would be the same as that required for filling any other ring, and that therefore, as adsorption progresses, the rate at which the gas is adsorbed would be proportional only to the length of the successive boundaries of the puddles. There is an obvious lack in this assumption - - to be met later - - for the time of filling a ring must vary inversely as the pressure of the gas, so that at lower pressures the time will be greater.

In the case used for the illustration the rate of sorption will increase up to the ninth ring of the diagram. From that time the length of the boundary will begin to decrease as the puddles run into each other. A sufficiently large area is to be taken so that a great number of such centers exist, and after the ninth ring the number of figures like ABCD can be taken as equal to the number of nuclear



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centers.

It is evident that the number of molecules adsorbed in a given circle (see Figure 7) will be proportional to the length of the boundary. Therefore, in the early stages of adsorption, or for circles from 0 to C, the number of molecules in the  $n$ th circle will be  $2\pi u n d$ , where  $u$  is the number of molecules adsorbed per unit length,  $d$  is the distance between rings (effective diameter of molecules) and  $n$  is an integer representing the number of the ring, counting from the center 0.

The above holds only when  $n d < 0 C$

To determine the number of atoms on a boundary where  $n d > 0 C$ , we proceed as follows:

Consider the portion of the figure bounded by  $\triangle L O C$ . The problem resolves itself into the determination of the lengths of arcs  $\overline{GH}$ ,  $\overline{IJ}$ , etc.

Consider  $\overline{GH}$ . Let it be an arc of circle  $n$ , whose radius is  $\overline{OH}$ . (The first arc is chosen to simplify the figure, but the proof is general.)

Then

$$\frac{\overline{OC}}{n d} \text{ equals } \cos \overline{H O C} \text{ where } d \text{ is the constant}$$

distance between circles as before, and  $\overline{OC}$  is half the constant distance between centers. Then  $n$  and  $\overline{H O C}$  are the only variables.



centers.

It is evident that the number of molecules adsorbed in a given circle (see Figure V) will be proportional to the length of the boundary. Therefore, in the early stages of adsorption, or for circles from 0 to  $c$ , the number of molecules in the  $n$ th circle will be  $2\pi n d$ , where  $n$  is the number of molecules adsorbed per unit length,  $d$  is the distance between rings (effective diameter of molecules) and  $n$  is an integer representing the number of the ring, counting from the center 0.

The above holds only when  $n d < c$ .

To determine the number of atoms on a boundary where

$n d > c$ , we proceed as follows:

Consider the portion of the figure bounded by  $dL$  0  $c$ .

The problem resolves itself into the determination of the

lengths of arcs  $\overline{GH}$ ,  $\overline{IL}$ , etc.

Consider  $\overline{GH}$ . Let it be an arc of circle  $n$ , whose

radius is  $\overline{O'G}$ . (The first arc is chosen to simplify the

figure, but the proof is general.)

Then

$$\frac{\overline{GH}}{n d} \text{ equals } \cos \overline{H'G'U} \text{ where } d \text{ is the constant}$$

distance between circles as before, and  $\overline{O'G}$  is half the

constant distance between centers. Then  $n$  and  $\overline{H'G'U}$  are the

only variables.



$$\frac{\pi}{4} - \angle HOC = \phi$$

$$\overline{GH} = n_1 \phi d$$

$$\text{or} \\ \overline{GH} = n_1 d \left( \frac{\pi}{4} - \arccos \frac{\overline{OC}}{n_1 d} \right)$$

Considering now a very large area with a large number of condensing centers, we may assume without appreciable error that there are as many figures of the ABCD sort possible as there are points P, O, Q, R.

Then

$$L = 8nd \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right),$$

where L is the length of exposed boundary of the nth circle. ( $nd > OC$ )

And letting u equal the number of adsorbed molecules per unit length as before,

$$uL = 8und \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right)$$

where uL is the number of molecules which may be adsorbed on the exposed boundary of the nth circle. ( $nd > OC$ )

Now let U equal the total number of molecules adsorbed by a given time. Then

$$U = \sum_{n=0}^{n=n_r} 2\pi n u d + \sum_{n=n_r+1}^{n=n_L} 8und \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right)$$

If we let

$$2\pi u d = k$$

$$U = \sum_{n=0}^{n=n_r} kn + \sum_{n=n_r+1}^{n=n_L} \frac{4nk}{\pi} \left( \frac{\pi}{4} - \arccos \frac{n_r d}{nd} \right)$$

where  $n_r$  is the number of the ring when  $nd = OC = (n_r d)$ .



$$\frac{\pi}{4} - \angle HOC = \phi$$

$$GH = n, \phi d$$

$$GH = nd \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right)$$

Considering now a very large area with a large number of condensing centers, we may assume without appreciable error that there are as many figures of the ABCD sort possible as there are points P, O, Q, R.

Then

$$L = 2nd \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right)$$

where L is the length of exposed boundary of the nth circle. ( $nd > OC$ )

And letting n equal the number of adsorbed molecules

per unit length as before,

$$uL = 2nnd \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right)$$

where u is the number of molecules which may be adsorbed on the exposed boundary of the nth circle. ( $nd > OC$ )

Now let U equal the total number of molecules

adsorbed by a given time. Then

$$U = \sum_{n=0}^{n_p} 2\pi nnd + \sum_{n=n_p+1}^{n=\infty} 2\pi nnd \left( \frac{\pi}{4} - \arccos \frac{OC}{nd} \right)$$

If we let  $2\pi nd = k$

$$U = \sum_{n=0}^{n_p} kn + \sum_{n=n_p+1}^{n=\infty} \frac{4nk}{\pi} \left( \frac{\pi}{4} - \arccos \frac{nd}{n_p d} \right)$$

where  $n_p$  is the number of the ring when  $nd = OC$  ( $n_p d$ ).



TABLE B

Using equation (1) the value of U may be computed in terms of K. This is done in the following table, using the simple case shown in the diagram.

I	II	III	IV
n	No. of atoms in ring	$U = \Sigma$ of Col- umn II	No. of atoms not yet adsorbed (53K - U)
0	0	0	53 K
1	K	K	52 K
2	2K	3K	50 K
3	3K	6K	47K
4	4K	10K	43K
5	5K	15K	38K
6	6K	21K	32K
7	7K	28K	25K
8	8K	36K	17K
9	9K	45K	8K
10	$\frac{40K}{\pi} (\frac{\pi}{4} - \cos^{-1} \frac{9}{10}) = 4.25K$	49.25K	4K
11	$\frac{44K}{\pi} (\frac{\pi}{4} - \cos^{-1} \frac{9}{11}) = 2.45K$	52K	K
12	$\frac{48K}{\pi} (\frac{\pi}{4} - \cos^{-1} \frac{9}{12}) = 1.00K$	53K	0
13	Impossible		



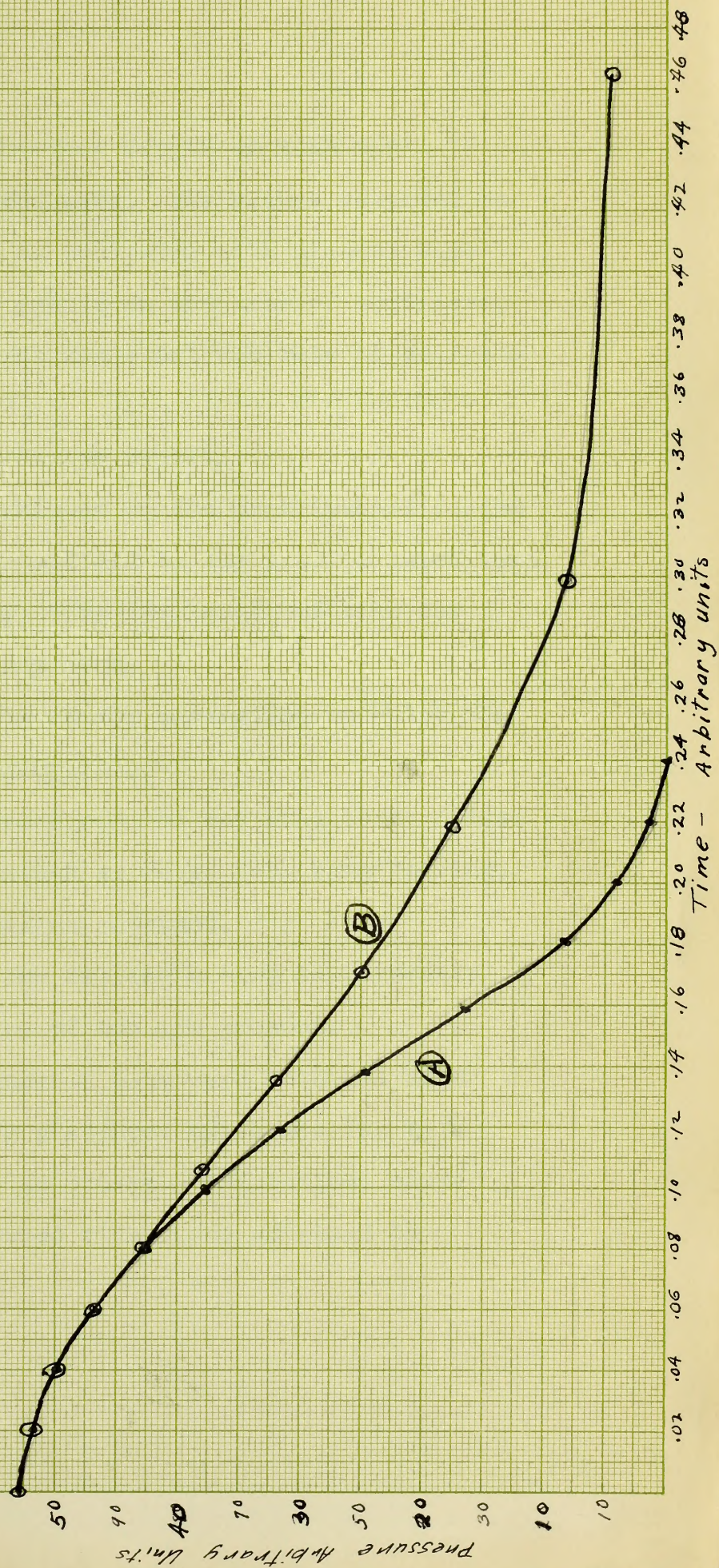
TABLE B

Using equation (1) the value of U may be computed in terms of K. This is done in the following table, using the simple case shown in the diagram.

n	No. of atoms in ring	U = $\sum$ of Col- umn II	No. of atoms not yet absorbed
			(22K - U)
I	0	0	22K
II	1	K	21K
III	2	2K	20K
IV	3	3K	19K
	4	4K	18K
	5	5K	17K
	6	6K	16K
	7	7K	15K
	8	8K	14K
	9	9K	13K
	10	$\frac{40K}{11} - \cos \frac{1}{10} = 3.52K$	12.48K
	11	$\frac{44K}{12} - \cos \frac{1}{11} = 3.65K$	11.35K
	12	$\frac{48K}{13} - \cos \frac{1}{12} = 3.78K$	10.22K
13	Impossible		0



Figure 8









If we now assume that the length of time for adsorption on any ring is the same, the values computed in Column IV will, if plotted as ordinates with unequal time intervals as corresponding points on the axis of abscissae, give a curve whose form might represent the rate of decrease in the unadsorbed gas.

Figure 8, curve A, is the result.

It bears some resemblance to the experimental curves but is faulty in the lower part and in any case is based upon a faulty assumption; namely, that the length of time for adsorption is the same on any ring.

We will replace this faulty assumption on which the curve was based, by two assumptions:

1. That the time required for any ring to be filled with adsorbed gas is a constant as we go from ring to ring, as long as the pressure remains constant.
2. That the time for filling a ring is inversely proportional to the pressure of the gas present.

Now, as our experimental data were obtained under the condition of decreasing pressure, allowance for this fact must be made in order to obtain a theoretical curve which may properly be compared with those obtained by experiment.



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Since the pressure is directly proportioned to the number of molecules of unadsorbed gas (TABLE C, COLUMN IV) we may immediately compute the time for filling a given ring as shown in the table below, letting  $K=1$  , for convenience.

The resulting curve B is shown in Figure 8. It offers a striking resemblance to the experimental curves presented in Figure 6.

TABLE C

I	II	III	IV
n	No. of atoms not sorbed (Table B)	Length of time for this ring	Total elapsed time
0	53	0	0
1	52	$\frac{1}{(53+52)\frac{1}{2}} =$	.019
2	50	$\frac{1}{(52+50)\frac{1}{2}} =$	.0196
3	47	etc.	.0206
4	43		.0222
5	38		.0246
6	32		.0286
7	25		.0350
8	17		.0475
9	8		.0800
10	4		.1666
11	1		.4000
12	0	2.0000	2.8637



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TABLE C

I	II	III	IV
n	No. of atoms not scored (Table B)	Length of time for this ring	Total elapsed time
0	52	0	0
1	52	$= \frac{1}{(52+52)^{\frac{1}{2}}}$	.019
2	50	$= \frac{1}{(52+50)^{\frac{1}{2}}}$	.0386
3	47	etc.	.0592
4	43		.0814
5	38		.1060
6	32		.1346
7	25		.1696
8	17		.2171
9	8		.2971
10	4		.4237
11	1		.8237
12	0		2.8837



## S U M M A R Y

1. The sorption curve, pressure vs. time, was obtained for air, nitrogen and hydrogen. The major part of the work was devoted to the study of hydrogen. Charcoal was the sorbent material. Sorption took place at the temperature of liquid oxygen.

2. Curves found for hydrogen are, under certain conditions, convex upward over a part of their length.

3. It was found for these cases that in some manner the adsorption of some of the gas acted upon the surface of charcoal so that the rate of sorption increased with time.

4. This can only be explained as due either to (a), a change in structure of the carbon surface due to the action of the adsorbed gas, or to (b), a greater likelihood of adsorption of gas by gas than of gas by charcoal.

5. The second (b) explanation seems more in accord with experience as, for instance, in the case of condensation of a supersaturated vapor. Following out this theory the growth of "puddles" of gas on the charcoal surface is proposed as the way in which the adsorption progresses.



# SUMMARY

1. The sorption curve, pressure vs. time, was obtained for air, nitrogen and hydrogen. The major part of the work was devoted to the study of hydrogen. Charcoal was the sorbent material. Sorption took place at the temperature of liquid oxygen.
2. Curves found for hydrogen are, under certain conditions convex upward over a part of their length.
3. It was found for these cases that in some manner the adsorption of some of the gas acted upon the surface of charcoal so that the rate of sorption increased with time.
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5. The second (b) explanation seems more in accord with experience as, for instance, in the case of condensation of a superheated vapor. Following out this theory the growth of "puddles" of gas on the charcoal surface is proposed as the way in which the adsorption progresses.



6. A theoretical pressure-time curve was drawn for an ideal process of the type suggested in 5. Its shape was found to resemble closely that of certain of the curves obtained experimentally; namely, those in which precautions had been taken to secure a charcoal surface initially nearly free from adsorbed gas.

7. This agreement is interpreted as a further justification of the theory that

Adsorption of hydrogen by charcoal takes place as a growth of "puddles" of gas, rather than promiscuously over the whole surface of the charcoal.



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7. This agreement is interpreted as a further

justification of the theory that

Absorption of hydrogen by

charcoal takes place as a growth of "bubbles" of gas, rather than promiscuously over the whole surface of the charcoal.



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ICA BOND











A U T O B I O G R A P H Y

I was born April 1, 1891 in Chardon, the county seat of Geauga County, near Cleveland, Ohio. My mother's maiden name was Martha Thomas. She was of a family that had come from South Wales and settled in northern Ohio in the 1840's. My father, Rev. Thomas Davis Phillips, was also of Welsh descent, his parents having migrated from North Wales to central New York State. His training for the ministry had been at Oberlin Theological Seminary, and at the time of my birth and for many years he was pastor of the Congregational Church at Chardon. I was the youngest of six children.

My elementary school work and most of my high school education was received in Chardon - - for short periods I attended Lincoln High School and West High School of Commerce at Cleveland. In the fall of 1910 I entered Rollins College, Winter Park, Florida, remaining there one year. For two years following, family circumstances made it necessary for me to teach and I held a position in York Township High School, Mallet Creek, Ohio.



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I enrolled at Oberlin College in 1913 as a Sophomore. My college work was again interrupted the next year and I became supervising principal at Doylestown, Ohio, for the year. However, by attending summer sessions at Wooster College, Case School of Applied Science and Oberlin College, and by carrying extra work at Oberlin, 1915-1916, I was enabled to receive the degree of Bachelor of Arts from Oberlin in 1916 and was later elected to Phi Beta Kappa as of the Class of 1916.

After graduation my first teaching was in Empire Junior High School, Cleveland. Early in 1917 I accepted a position as teacher of physics and general science at the Johnstown, Pennsylvania, High School. With the exception of time spent in United States Army service, during 1918, I remained in Johnstown until 1920, and had become head of the physical sciences department.

In September 1920 I began teaching in the Physics Department of Marietta College. I attended the summer sessions of the University of Michigan, 1921, 1922 and 1923, and in 1923 was granted the degree of Master of Science from that University. In 1924 I was advanced to assistant professorship at Marietta College



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I was married on December 25, 1916 to Josephine Elvira Frye, of Oberlin College. We have three daughters, aged 15, 13 and 7.

I hold membership in The American Physical Society and The Optical Society of America. I am vice president of The Central Ohio Physics Club, an organization of teachers of Physics in the Ohio colleges. I am a fellow in the American Association for the Advancement of Science.



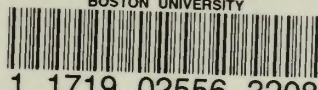
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